

ULTRA NANOINDENTATION TEST OF INJECTION POLYBUTYLENE TEREPHTHALATE (PBT) IRRADIATED BY LOW DOSES BETA IRRADIATION

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The influence of high doses of beta radiation on the changes in the structure and selected properties (mechanical and thermal) polymers were proved. Using high doses of beta radiation for polybutylene terephthalate (PBT) and its influence on the changes of mechanical properties of ultra nanohardness has not been studied in detail so far. The specimens of polybutylene terephthalate (PBT) were made by injection moulding technology and irradiated by high doses of beta radiation (0, 33, 66 and 99 kGy). The changes in the microstructure and micromechanical properties of surface layer were evaluated using FTIR, WAXS and instrumented ultra nanohardness test. The results of the measurements showed considerable increase in mechanical properties (indentation hardness, indentation elastic modulus) when the high doses of beta radiation are used.

KEYWORDS

polybutylene terephthalate (PBT), microhardness, mechanical properties, β -irradiation, FTIR, WAXS

1 INTRODUCTION

Cross-linking is a process in which polymer chains are associated through chemical bonds. Cross-linking is carried out by chemical reactions or radiation and in most cases the process is irreversible. Ionizing radiation includes high-energy electrons (electron beam - β -rays) (Fig. 2). These not only are capable of converting monomeric and oligomeric liquids into solids, but also can produce major changes in properties of solid polymers [Woods 1974, Barlow 1979].

The engineering polymers are a very important group of polymers which offer much better properties in comparison to those of standard polymers. Both mechanical and thermal properties are much better than in case of standard polymers. The production of these types of polymers takes less than 1 % of all polymers (Fig. 1).

Poly (butylene terephthalate), PBT, is a commercially important engineering polymer with a wide range of applications such as injection molding and extrusion. As a member of the polyester family, it is also often used as the matrix material in glass fiber reinforced composites, having attractive mechanical properties, good moldability and fast crystallization rate [Pharr 1998]. PBT has some processing advantages over its chemical relative, poly (ethylene terephthalate), PET. The melting temperature of PBT is about 230°C, which is lower than PET, (ca. 270°C), allowing PBT to be processed at lower temperatures. In addition, PBT

has a lower glass transition temperature, a faster crystallization rate.

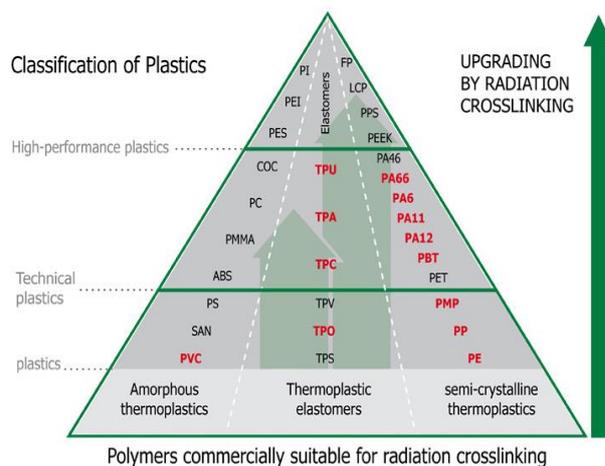


Figure 1. Upgrading by radiation cross-linking of PBT

The irradiation cross-linking of thermoplastic materials via electron beam or cobalt 60 (gamma rays) proceeds separately after the processing. The cross-linking level can be adjusted by the irradiation dosage and often by means of a cross-linking booster [Zamfirova 2010, Dobransky 2016].

The main difference between β - and γ - rays is in their different abilities of penetrating the irradiated material. γ - rays have a high penetration capacity. The penetration capacity of electron rays depends on the energy of the accelerated electrons [Ovsik 2012].

The thermoplastics which are used for production of various types of products have very different properties. Standard polymers which are easy obtainable with favourable price conditions belong to the main class. The disadvantage of standard polymers is limited both by mechanical and thermal properties [Ovsik 2014]. The group of standard polymers is the most considerable one and its share in the production of all polymers is as high as 90%.

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High performance polymers have the best mechanical and thermal properties but the share in production and use of all polymers is less than 1%.

Common PBT, when exposed to the effect of the radiation cross-linking, degrades and its mechanical properties deteriorate. Using cross-linking agent TAIC (triallyl isocyanurate) produces a cross-linking reaction inside the PBT structure. The utility properties of PBT improve when the noncrystalline part of PBT is cross-linked [Ragan 2012].

The present work deals with the influence of morphology on the microhardness of irradiated crosslinked PBT.

The aim of this paper is to study the effect of ionizing radiation with low doses beta irradiation, on mechanical properties of surface layer of polybutylene terephthalate (PBT) and compare these results with those of non-irradiated samples [Oliver 2004, Behalek 2013].

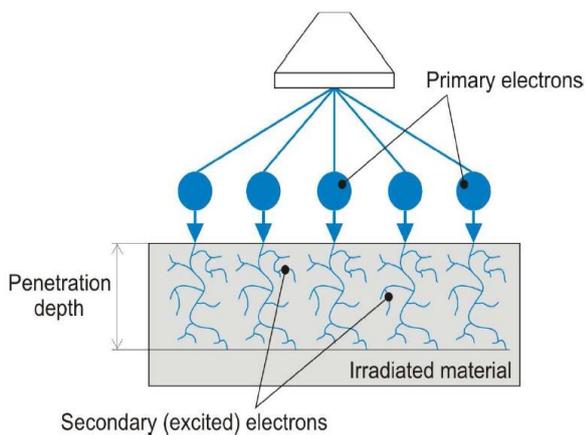


Figure 2. Design of Electron rays

Experimental section

1.1 Material and methods

For this polybutylene terephthalate (PBT) V-PTS-CREATEC-B3HZC * M800/25 nature; PTS Plastics Technologie Service, Germany) was used. Irradiation was carried out in the company BGS Beta Gamma Service GmbH & Co, KG, Saal an der Donau, Germany with the electron rays, electron energy 10 MeV, doses minimum of 0, 33, 66 and 99 kGy on air by the ambient temperature (Fig. 3).

The samples were made using the injection moulding technology on the injection moulding machine Arburg Allrounder 420C. Processing temperature range 210–240 °C, mold temperature 50 °C, injection pressure 80 MPa, injection rate 50 mm/s.

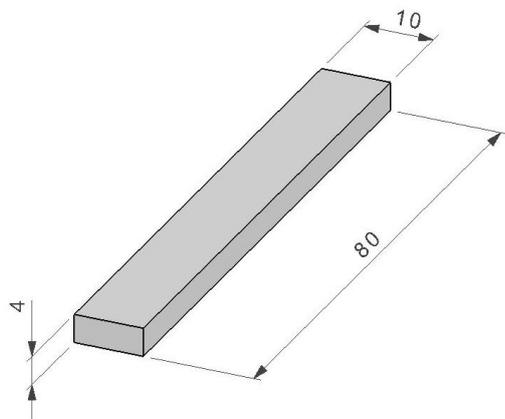


Figure 3. Dimension of sample

1.2 Ultra nanoindentation test

Nano-indentation test were done using a Ultra Nano indentation Tester (UNHT) (Fig. 5), CSM Instruments (Switzerland) according to the CSN EN ISO 14577. Load and unload speed was 1000 $\mu\text{N}/\text{min}$. After a holding time of 90 s at maximum load 500 μN the specimens were unloaded [Manas 2015, Ovsik 2015]. The specimens were glued on metallic sample holders (Fig. 3).

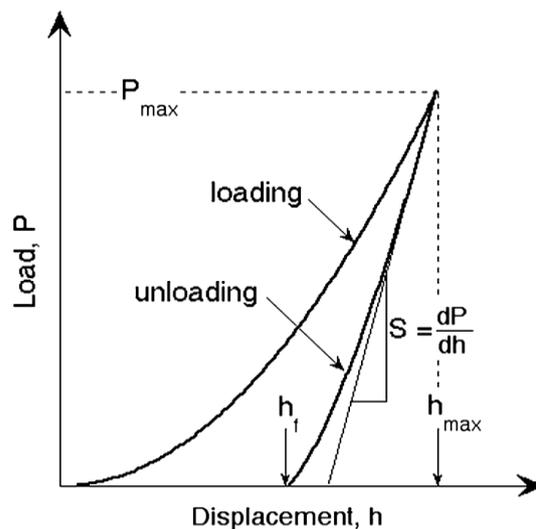


Figure 4. Schematic illustration of indentation curve

$$H_{IT} = \frac{F_{\text{max}}}{A_p} \quad (1)$$

$$E_{IT} = E^* \cdot (1 - \nu_s^2) \quad (2)$$

The indentation hardness (H_{IT}) was calculated as maximum load (F_{max}) to the projected area of the hardness impression (A_p) and the indentation modulus (E_{IT}) is calculated from the Plane Strain modulus (E^*) using an estimated sample Poisson's ratio (Fig. 4).



Figure 5. Ultra Nanoindentation tester

1.3 Wide-angle X-ray scattering

Wide-angle X-ray diffraction patterns were obtained using a PANalytical X'Pert PRO X-ray diffraction system (Netherlands). The $\text{CuK}\alpha$ radiation was Ni-filtered. The scans ($4.5^\circ \cdot 2\Theta/\text{min}$) in the reflection mode were taken in the range $5\text{--}30^\circ \cdot 2\Theta$. The sample crystallinity (X) was calculated from the ratio of the crystal diffraction peaks and the total scattering areas. Crystall size L110 of α most intensive peak at 110 was calculated using Scherrer equation. As a standard "perfect" crystal terephthalic acid with the peak at $2\Theta = 17.4^\circ$ and the half maximum breadth $0.3^\circ \cdot 2\alpha$ was chosen.

1.4 Fourier transformed infrared spectroscopy (FTIR)

Infrared spectra were measured by ATR technology using single reflection ATR (GladiATR, PIKE Technologies), which was equipped with diamond crystal of refractive index of 2.4 and impact angle 45°. Spectra were measured by FTIR spectrometer Nicolet 6700 FTIR (Thermo Nicolet Instruments Co., Madison, USA) blown with dry air. Spectra were measured at the definition of 2 cm⁻¹ using 64 scans. Pure ATR diamond crystal was used for the background and ATR correction was used for the adjustment of spectra. Manipulation with spectra was done using OMNIC Software 8.2. Each specimen was measured 2 times on each side.

2 RESULTS AND DISCUSSION

The development of micromechanical properties of irradiated polybutylene terephthalate (PBT) was characterized by the instrumented test of ultra nanohardness, as can be seen in Fig. 6. The highest values (141 MPa) of indentation hardness (H_{IT}) were found at 33 kGy radiation dose. The lowest value of indentation hardness was found on non-irradiated polybutylene terephthalate (PBT) (117 MPa). Lower value of indentation hardness (130 MPa) was measured for polybutylene terephthalate (PBT) modified by the radiation dose of 66 kGy. The increase of indentation hardness at 33 kGy radiation dose was by 20 % compared to the non-irradiated polybutylene terephthalate (PBT).

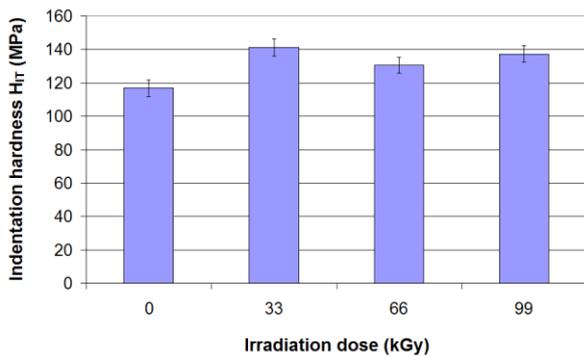


Figure 6. Indentation hardness H_{IT} of PBT vs. irradiation doses

Similar development was recorded for stiffness of specimens represented by the indentation elastic modulus (E_{IT}) illustrated in Fig. 7.

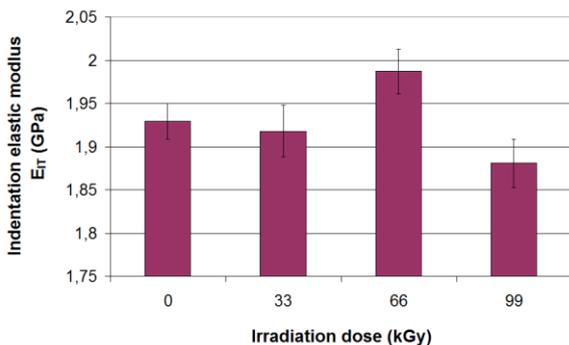


Figure 7. Indentation elastic modulus E_{IT} of PBT vs. irradiation doses

The results of measurements show clearly that the lowest values of stiffness were measured polybutylene terephthalate (PBT) irradiated by 99 kGy dose (1.88 GPa), while the highest values were reached in polybutylene terephthalate (PBT) irradiated by 66 kGy dose (1.98 GPa). Lower value of indentation elastic modulus (0.26 GPa) was measured on non-

irradiated polybutylene terephthalate (PBT). A significant increase of stiffness (2 %) was recorded at the radiation dose of 66 kGy compared to the non-irradiated polybutylene terephthalate (PBT).

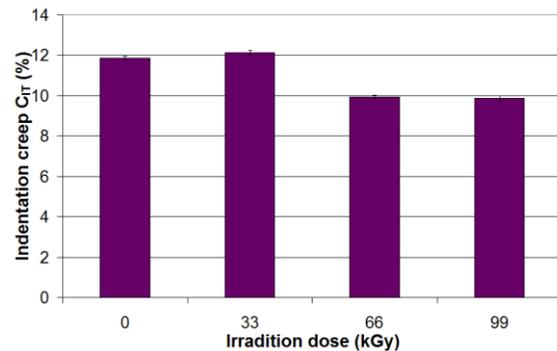


Figure 8. Indentation creep C_{IT} of PBT vs. irradiation doses

Plastic (W_{plast}) and elastic (W_{elast}) deformation measured during ultra nanohardness test also showed (Fig. 9) that the lowest values of plastic deformation work were measured at the radiation dose of 99 kGy, while the highest values of plastic deformation work were for polybutylene terephthalate (PBT) modified by the radiation dose of 33 kGy. This was also confirmed (Fig. 9) by the results of measurements of reverse relaxation coefficient (η_{IT}).

Sample	X x-ray, %, ±1%
0 kGy	31
33 kGy	29
66 kGy	33
99 kGy	31

Table 1. X-ray diffraction of non-irradiated and irradiated PBT

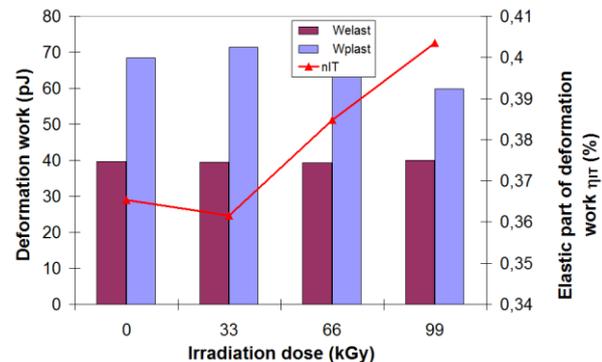


Figure 9. Deformation work of PBT vs. irradiation doses

Material deformation in time under constant stress (indentation creep) measured by instrumented test of ultra nanohardness showed (Fig. 8) that the highest creep values were measured on non-irradiated polybutylene terephthalate (PBT) (12.14 %), while the lowest creep value was found polybutylene terephthalate (PBT) irradiated by 99 kGy dose (9.86 %). The creep dropped by 17 % as a result of radiation, which represents a considerable increase of surface layer resistance.

Radiation, which penetrated through specimens, gradually formed cross-linking (3D net), first in the surface layer and then in the total volume, which resulted in considerable changes in specimen behavior. 3D net together with crystalline phase caused changes mainly in the surface layer, which led to a

significant increase of indentation hardness and stiffness of surface layer. This caused higher resistance of surface layer to wear, scratch, etc. Also, the creep values decreased as a result of changes made after the specimens were subjected to beta radiation.

The Figure 10 shows typical X-ray diffraction spectrum of the non-irradiated and irradiated polybutylene terephthalate. There is an apparent presence of α -phase in the non-irradiated specimen. The greatest grow of α -phase is seen at the radiation dose of 99 kGy (Fig. 10).

When applying β -radiation the structure of polypropylene undergoes loss and then a grow of the crystalline phase. It can be assumed that the size of individual crystals will correspond with the loss of crystalline phase (crystalline value X calculated lay in the range 29-33 %). Cross-linking occurs in the remaining noncrystalline part which has a significant influence on the mechanical properties of the surface layer. The greatest size of crystalline phase was found in the case at the radiation dose of 66 kGy (33 %). The lowest size of crystalline phase was found in the case at the radiation dose of 99 kGy (31 %). On the contrary the smaller size of crystalline phase was measured at non-irradiated (31 %). Its influence on the mechanical behavior is insignificant.

The infra-red spectroscopy, IR, is the versatile method to follow chemical modifications in a polymeric material. Studies carried through by some researchers, presented the formation of carbonyl groups.

The results of the infrared spectroscopy showed changes of relative representation of carbonyl groups in relation to the radiation dose (Fig. 11).

When the specimen is irradiated, it leads to oxidation on C-H bonds and formation of oxygenic functional groups.

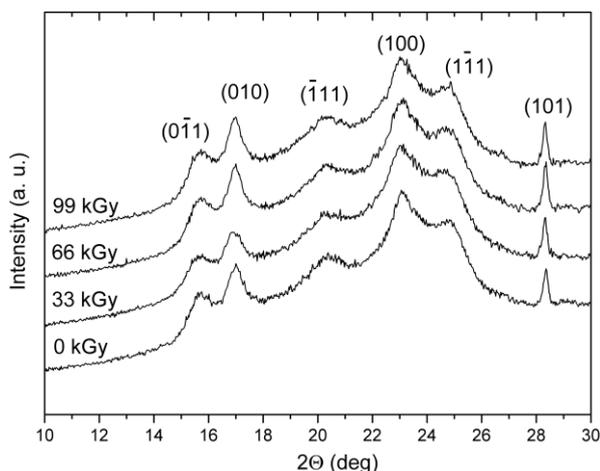


Figure 10. X-ray diffraction of non-irradiated and irradiated PBT

Differential spectra of PBT specimens in the area of 1850 – 1200 cm^{-1} . Spectra are dominated by bands of valence vibrations of C=O of bonds of carboxyl groups at $\sim 1700 \text{ cm}^{-1}$ and C-O at 1265 cm^{-1} . Negative bands of small intensity at 1472 and 1462 cm^{-1} belong to deformation vibrations of aliphatic C-H bonds.

Change in relative abundance of carbonyl groups depending on the radiation dose of PBT. Changes in the content of carbonyl groups were expressed by the ratio between the band area in $1800\text{-}1500 \text{ cm}^{-1}$ and the band area of valence vibrations of aliphatic C-H bonds in $3000\text{-}2700 \text{ cm}^{-1}$.

The smallest values of relative change of representation of carbonyl groups were found at radiation dose of 0 kGy. At this dose the worse values of mechanical properties of the tested polybutylene terephthalate (PBT) were measured. The greatest change was found at radiation dose of 99 kGy. These changes of the structure correspond with the changes of mechanical properties of modified polybutylene terephthalate (PBT) beta radiation.

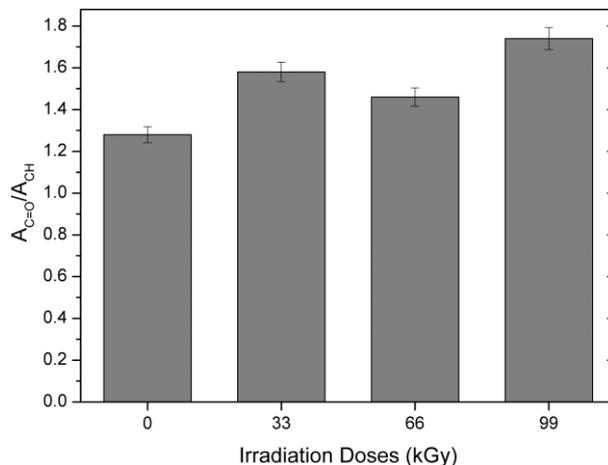


Figure 11. Change in the relative representation of carbonyl groups of PBT in relation to the irradiation doses

Higher radiation dose does not influence significantly the nano-hardness value. An indentation hardness increase of the surface layer is caused by irradiation cross-linking of the tested specimen. A closer look at the ultra nano-hardness results reveals that when the highest radiation doses are used, ultra nano-hardness decreases which can be caused by radiation induced degradation of the material.

3 CONCLUSIONS

The experimental study deals with the effect of modification of the surface layer by irradiation cross-linking on the properties of the surface layer of polybutylene terephthalate (PBT). Polybutylene terephthalate (PBT) was modified by beta irradiation at doses of 0, 33, 66 and 99 kGy. The changes of micromechanical properties were found at the radiation doses of 33 and 66 kGy for indentation hardness and elastic modulus (which increased by 32% and 16%) compared to the non-irradiated polybutylene terephthalate (PBT). Improvement of mechanical properties in micro and macro scale of radiated low density polyethylene has a great significance also for industry. The modified low density polyethylene shifts to the group of materials which have considerably better properties. Its micromechanical properties make low density polyethylene ideal for a wide application in the areas where higher resistance to wear, scratch are required.

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